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(21) International Application Number: PCT/US92/08133 (22) International Filing Date: 25 September 1992 (25.09.92) (30) Priority data: 765,647 25 September 1991 (25.09.91) US (71) Applicant: RESEARCH CORPORATION TECHNOLOGIES, INC. [US/US]; 6840 East Broadway Boulevard, Tucson, AZ 85710 (US). (72) Inventors: SUSLICK, Kenneth, S. ; 63 Chestnut Court, Champaign, IL 61821 (US). GRINSTAFF, Mark, E. ; 505 South Mathews Box 48, Urbana, IL 61801 (US). CICHOWLAS, Andrzej, A. ; 1960 A Orchard Street, Urbana, IL 61801 (US). CHOE, Seok-Burm ; Dalso-Ga Sindang-Dang 1000, Taegu, 704-701 (KR).		(74) Agent: SCOTT, Anthony, C.; Scully, Scott, Murphy and Presser, 400 Garden City Plaza, Garden City, NY 11530 (US). (81) Designated States: AU, CA, JP, KP, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, SE). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: THE SONOCHEMICAL SYNTHESIS OF AMORPHOUS METALS (57) Abstract The present invention relates to novel substantially pure amorphous metals and the sonochemical synthesis thereof comprising irradiating volatile organometallic compounds with high intensity ultrasound. The present invention is further directed to the use of amorphous metals as reactive catalysts for various processes such as the Fischer-Tropsch hydrogenation of carbon monoxide and for the hydrogenolysis and dehydrogenation of saturated hydrocarbons. The present invention further relates to the use of these amorphous metals as soft ferromagnetic materials. <div style="text-align: center; margin-top: 100px;">W</div>		

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THE SONOCHEMICAL SYNTHESIS OF AMORPHOUS METALS

The present invention relates to the novel synthesis of amorphous metals, metal powders, or metallic glasses, and uses thereof in a variety of applications, with such applications being their use as a catalytic material and their use as a soft magnetic material. The present invention further relates to the sonochemical synthesis of these novel amorphous metals through the application of high intensity ultrasound to volatile organometallic or inorganic compounds. More particularly, this invention is directed to the synthesis of substantially pure amorphous iron and its use as a highly active catalyst for the Fischer-Tropsch hydrogenation of carbon monoxide and for hydrogenolysis and dehydrogenation of saturated hydrocarbons.

Amorphous materials are those materials which lack an ordered crystalline structure. This property is characteristic of liquids, in which the molecules do not have long range order in their atomic positions. All simple liquids are amorphous. A solid material, on the other hand, characteristically exhibits a molecular or atomic lattice structure which gives it a well-defined structural order over distances long compared to atomic dimensions.

There are however, exceptions. Some materials, although being solid, do not have long range order in the structure of their component atoms. When a solid melts, it changes from the crystalline to the amorphous state. The melted material remains in the amorphous state until recrystallization takes place. Silica glass, an example of an amorphous solid material, does not recrystallize because of its exceptionally high viscosity on cooling.

Thus, glass retains the amorphous nature of a liquid even though it is physically rigid.

Metallic glasses, or amorphous metals or metal alloys, are metals or metal alloys having an amorphous atomic structure analogous to that of silica glass, thus the origin of the terms "metallic glasses" and "glassy metals". These amorphous structures, as previously explained, lack long range crystalline order. Metallic glasses can be obtained by subjecting a molten metal or alloy to extremely rapid cooling or quenching. The molten material is cooled so rapidly that a crystalline structure is prevented from being formed. The vitreous material which is produced is predominantly amorphous and exhibits unique combinations of properties that make it capable of various applications. Some known amorphous materials have exceptionally high mechanical strength and still maintain some ductility, some are exceedingly corrosion resistant and others are excellent soft magnetic materials.

A number of important industrial applications of amorphous materials are being developed based on their unique properties. Amorphous metals are often soft ferromagnets and as such have the potential to be used in the recording and magnetic tape industry, and more specifically in connection with magnetic read/write recording heads. Glassy metals can exhibit permeability comparable to, or higher than Permalloy, yet they are mechanically tough and not easily deformed.

A related commercial development of amorphous metals is their use in power transformer cores. Amorphous metals with their high permittivity could replace the current transformer materials and greatly improve the energy efficiency of such power devices.

Amorphous materials lack grain boundaries and are consequently often chemically robust, making their use as protective coatings and materials in corrosive chemical environments such as acid batteries, sea water, etc., very beneficial.

Amorphous metals also have the potential to be reactive catalysts for the petroleum and chemical industries. The Fischer-Tropsch process, for example, converts synthesis gas, initially produced by the gasification of coal with steam and oxygen, to largely aliphatic hydrocarbons over an iron or cobalt catalyst. Other processes such as dehydrogenation and hydrogenolysis are also used heavily in this area. Currently, commercially available crystalline iron powders are used as catalysts.

Although some of the applications of metallic glasses are well established, the cost and stability of these materials still present major problems. For a more in depth review of amorphous metallic alloys and their structure and uses, see Anatharaman, T.R. Metallic Glasses (Trans Tech Publication, Aedermannsdorf, Switzerland, 1984); Haasen, P. and Jaffee, R.I. Amorphous Metals And Semiconductors (Pergamon Press, London, 1986); and Steeb, H. and Warlimont, H., eds. Rapidly Quenched Metals (Elsevier Science, Amsterdam, 1985).

Currently, amorphous metallic alloys are produced using expensive and technically difficult methods that involve the splattering of molten metals onto cold surfaces and the rapid cooling thereof with techniques such as gun, roller, or splat quenching. An extensive patent literature exists for such techniques. It is to be noted, however, that amorphous materials produced by these methods are generally alloys with two, three, or

more constituent elements. For example, all prior iron-containing metallic glasses contain large amounts of other alloying elements with greater than 20% being typical. See the aforementioned references along with Takashi, S. J. Matl. Sci. Lett. 6: 844 (1987) and Luborsky, F.E., ed. Amorphous Metallic Alloys (Butterworths, London, 1983).

In order to prevent crystallization in the synthesis of amorphous materials, extreme rapid cooling of molten metals is necessary. Cooling rates of about 10^5 to 10^7 degrees kelvin (K)/sec are required. As a comparative example, plunging red hot steel into water produces cooling at only about 2500 K/sec.

High intensity ultrasound can induce extraordinary local, transient heating in otherwise cool liquids, with subsequently enormous cooling rates, in excess of 10^9 K/sec. Ultrasound provides a unique interaction of energy and matter. For less than a few microseconds, it can produce in liquids an intense localized heating of 5500°C , almost the temperature at the surface of the sun.

As used herein, "high intensity ultrasound" is defined as ultrasound having sufficient intensity to create cavitation in a liquid. "Cavitation", meaning the formation, expansion, oscillation and compression of bubbles in a liquid, can occur in the presence of ultrasound or other turbulent flow. The exposure of a liquid to ultrasound is referred to as "irradiation" and the breaking of a chemical bond or bonds by the application of ultrasonic irradiation is known as "sonolysis". Consequently, the production or synthesis of a chemical or chemical material through the use of ultrasound is called "sonochemical synthesis".

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As indicated above, the chemical effects of ultrasound derive from the physical phenomenon of acoustic cavitation: the creation, growth, and implosive collapse of bubbles in liquids. If the sound field in a liquid is sufficiently intense, bubbles will form in the liquid during the expansion cycle. The oscillations of the sound field make these bubbles grow and contract. At a certain size, the bubbles can be driven into an implosive collapse. Because compression of a gas creates heat, this implosion generates an intense, but short lived, hot-spot. In essence, acoustic cavitation effectively concentrates energy by transferring the low energy density of sound into the high energy density of a collapsing bubble. Ultrasound is currently being used to enhance various chemical reactions. Such "sonochemistry" includes the creation of clean and highly reactive surfaces on metals and the initiation or enhancement of catalytic reactions.

The chemical effects of ultrasound are primarily derived from hot spots formed during acoustic cavitation. As stated earlier, this process serves to concentrate dramatically the low energy density of a sound field. Previous experiments established that the effective temperature reached during bubble collapse was approximately 5200 K with calculated hot spot lifetimes of around two microseconds. See Suslick, K.S. et al., J. Am. Chem. Soc. 106, 5641 (1986); Suslick, K.S. et al., IEEE Ultrason. Symp. Proc. 4, 1116 (1985); and Suslick, K.S. et al., IEEE Ultrason. Ferroelec. Freq. Cont. 33, 143 (1986). Consequently, heating and cooling rates during cavitational collapse are calculated to be greater than 2×10^9 K/sec. For more on the application of ultrasound to chemical synthesis, see Suslick, K.S.

Science 247, 1439 (1990); Suslick, K.S. Sci. Am. 260, 80 (February 1989); Einhorn, C. et al. Synthesis 11, 787 (1989); Lindley, J. et al. Chem. Soc. Rev. 16, 275 (1987); and Boudjouk, P. J. Chem. Ed. 63, 427 (1986). For more on useful experimental apparatus used in the application of ultrasound, see Suslick, K.S. et al. in Experimental Organometallic Chemistry: A Practicum in Synthesis and Characterization (eds. Wayda, A. and Darensbourg, M.Y.) 195-198 (American Chemical Society, Washington, D.C., 1987).

The present invention is directed to novel, substantially pure amorphous materials, both amorphous metals and amorphous metallic alloys, and their use as highly active heterogeneous catalysts.

The present invention is further directed to the process for making these novel amorphous materials which comprises using the conditions created by high intensity ultrasound to volatile organometallic or inorganic compounds.

One such amorphous metal obtained via the process of the present invention is amorphous iron. Substantially pure, i.e., at least 96%, amorphous iron was produced from the sonolysis of iron pentacarbonyl, $\text{Fe}(\text{CO})_5$. Because the present process uses volatile organometallic or inorganic compounds of broad scope, the number of pure amorphous metals and metal alloys which can be produced using the present technique can also be quite large. Other volatile organometallic or inorganic compounds besides $\text{Fe}(\text{CO})_5$ which can be used in the present process include, for example, a very large number of compounds; among these are: $\text{Cr}(\text{CO})_6$, $\text{Mo}(\text{CO})_6$, $\text{W}(\text{CO})_6$, $\text{Mn}_2(\text{CO})_{10}$, $\text{Ni}(\text{CO})_4$, TiCl_4 , $\text{Zr}(\text{BH}_4)_4$, $\text{Pd}(\text{allyl})_2$ and the like.

Figure 1 is a scanning electron micrograph of an amorphous iron powder synthesized by the process of the present invention, obtained on a Hitachi S800 electron microscope.

Figure 2 is a transmission electron micrograph of an amorphous iron powder synthesized by the process of the present invention, obtained on a Phillips EM400T electron microscope.

Figure 3 is a differential scanning calorimetry of an amorphous iron powder synthesized by the process of the present invention vs. a crystalline iron powder, obtained at 10°C/min. on a DuPont 1090 calorimeter.

Figure 4a shows the x-ray diffraction patterns of the amorphous iron powder synthesized by the process of the present invention before heat treatment.

Figure 4b shows the x-ray diffraction patterns of the amorphous iron powder of Figure 4a after crystallization at 350°C for six hours. Both Figures 4a and 4b were obtained on a Rigaku D-max diffractometer.

A new synthetic route to amorphous metals, for example, metal powders, has been found which yields substantially pure amorphous materials, the purity of which was not obtainable up to the present invention. Through the sonolysis of volatile organometallic and inorganic compounds, the novel amorphous metals of the present invention are formed. More specifically, the process of making an amorphous metal in accordance with the present invention comprises irradiating a volatile organometallic or inorganic compound with high intensity ultrasound for a time and under conditions sufficient to convert the organometallic or inorganic compound into the amorphous metal. Various volatile organometallic compounds may be used in the present process and include

metal carbonyls such as $\text{Fe}(\text{CO})_5$, $\text{Cr}(\text{CO})_6$, $\text{Mo}(\text{CO})_6$, $\text{W}(\text{CO})_6$, $\text{Mn}_2(\text{CO})_{10}$, and $\text{Ni}(\text{CO})_4$ and other volatile organometallic compounds such as $\text{Pd}(\text{allyl})_2$, etc. Examples of some volatile inorganic compounds which may be used in the present process are, for example, TiCl_4 and $\text{Zr}(\text{BH}_4)_4$. By applying high intensity ultrasound to these organometallic and inorganic compounds, the extreme temperatures created during acoustic cavitation strip the ligands from the metal.

The amorphous alloys of the present invention can be prepared from the ultrasonic irradiation of solutions containing two or more volatile organometallic or inorganic compounds as well as from solutions containing volatile organometallic or inorganic compounds and volatile main group compounds, wherein said main group compounds are compounds containing boron, carbon, nitrogen, silicon, phosphorus, sulfur, arsenic, selenium, antimony, tellurium or halide.

A preferred process includes the following steps:

(1) preparing a solution of the volatile organometallic or inorganic compound(s) in a low volatility solvent;

(2) flushing the resulting solution with an inert gas, preferably argon, in order to remove the oxygen therefrom;

(3) subjecting the deoxygenated solution to ultrasonic irradiation, for example by transferring said deoxygenated solution to a temperature controlled apparatus suitable for the ultrasonic irradiation of a liquid;

(4) applying the ultrasonic force for a time and under conditions sufficient to produce the desired yield, said particular conditions including but not

limited to the selected precursor(s) being used, the vapor pressure of the solvent, the vapor pressure of the inorganic or organometallic precursor(s) and the intensity of the ultrasound being applied; and

(5) separating the resulting liquid and solid under an inert atmosphere, for example, by filtering.

Vapor pressure of the reaction mixture plays an important roll in the acoustic cavitation step. The higher the total vapor pressure during this step, the lower the efficiency of bubble collapse and consequently the lower the effective peak cavitational temperature. It is at low vapor pressure that the process of the present invention is carried out. The higher cavitational temperature, which results from low vapor pressure, causes total ligand dissociation and the amorphous metals of the present invention are formed. In addition, the vapor of the inorganic or organometallic precursor should be as large a fraction of the total reaction mixture vapor as possible to enhance the yield and rate of amorphous metal formation.

Although a variety of solvents may be used in the present process with positive results, for optimum yield of the amorphous metals, it is best to utilize a low volatility or low vapor pressure solvent, i.e. a solvent having a vapor pressure approximately below 50 Torr or 0.1 atm. Thus, for example, although decane and pentane are very similar solvents, decane is preferred because it is a low vapor pressure solvent and consequently better results are obtained through the use of decane.

Other liquids are also potentially useful if these liquids are relatively non-reactive and have low vapor pressures under irradiation conditions. These include,

but are not limited to, aromatic liquids, ethers and polyethers, polysiloxanes, and molten salts.

Alkane solvents are especially useful in this process; these include saturated aliphatic hydrocarbons such as pentane, heptane, octane, decane and dodecane. Those solvents with a low vapor pressure under the reaction conditions employed herein during ultrasonic irradiation are preferred. Alkanes or other solvents that are solids at room temperatures may also be useful if the reaction is heated above their melting points.

To produce the highest temperature possible during cavitation, the choice of dissolved gas in the liquid reaction mixture is also important. Monatomic gases are preferred relative to diatomic which are preferred relative to polyatomic gases due to their effect on the heating process during gas compression. The thermal conductivity of the dissolved gas should be as low as practical. In addition, the reactivity of the dissolved gas must be considered; for example, in the presence of oxygen the formation of iron oxides will occur during ultrasonic irradiation of $\text{Fe}(\text{CO})_5$. For these reasons, xenon is preferred relative to krypton which is preferred relative to argon. In practice, argon offers an excellent compromise of cost and desirable properties.

The sonochemical synthesis of metallic glasses can be accomplished with low cost ultrasonic equipment. Gram quantities are easily prepared with simple laboratory ultrasonic sources of 400 W, and scale up with commercially available modular 20 kW industrial units can be readily achieved. In order to control the system vapor pressure, it is important that the reaction volume be controlled, e.g. thermostated.

As previously indicated, the products of the invention are substantially pure. "Substantially pure" as employed herein and in the appended claims means purity levels of at least about 90%, and usually above 95%. For example, amorphous iron powder produced in accordance with the present invention is of an order of purity in excess of 95%. Yields approaching the 100% purity level are contemplated.

The following example is provided to further illustrate the present invention.

EXAMPLE

Pure $\text{Fe}(\text{CO})_5$ or 4.0 M solutions in decane were irradiated at 0°C with a high intensity ultrasonic probe (Sonics and Materials, model VC-600, 0.5 in. Ti horn, 20kHz, 100 W/cm²) for three hours under an argon atmosphere. After irradiation, the iron powder produced was filtered and washed with dry pentane in an inert atmosphere box (Vacuum Atmospheres, <1 ppm O_2). Gram quantities of material were isolated. Elemental analysis of the amorphous iron powder, obtained as a dull black powder, showed it to be > 96% iron by weight, with a trace amount of carbon (3%) and oxygen (1%), presumably from the decomposition of alkane solvent or carbon monoxide during ultrasonic irradiation.

The amorphous nature of this iron powder was confirmed by several techniques, including scanning and transmission electron microscopy, differential scanning calorimetry, x-ray powder diffraction, and electron beam microdiffraction. Scanning electron micrographs of the iron powder obtained from the ultrasonic irradiation of $\text{Fe}(\text{CO})_5$ show conchoidal fractures, typical of a non-crystalline material (see Figure 1). High resolution transmission electron microscopy show no evidence for crystallite formation to below 4 nm (see Figure 2). Differential scanning calorimetry shows one large exothermic transition at 308°C corresponding to a disorder/order transition (i.e., crystallization) of the amorphous iron (see Figure 3).

Initial x-ray diffraction shows no diffraction peaks in the amorphous iron (see Figure 4a). After heat treatment of the amorphous iron under N_2 at 350°C (i.e., sufficient to induce crystallization), the lines characteristic of α -iron metal (d A 2.03, 1.43, 1.17,

1.04) were observed (see Figure 4b). After crystallization, the x-ray powder diffraction pattern contained no peaks attributable to iron carbide or other iron alloys, thus confirming the formation of essentially pure iron from ultrasonic irradiation of $\text{Fe}(\text{CO})_5$. Again it is noted that all prior iron-containing metallic glasses contain large amounts of other alloying elements, i.e., typically greater than twenty percent. Electron microdiffraction with a transmission electron microscope confirmed these observations and showed only a diffuse (111) ring characteristic of an amorphous material. After continued sample exposure to the electron beam and its consequent heating, the iron powder crystallized in situ and the diffraction rings from α -Fe were observed.

High resolution transmission electron micrographs reveal the microstructure of the amorphous iron powder (See Figure 2). The large particles shown in Figure 1 are composites of very small particles (10nm) with significant void volume. Surface areas were determined by BET gas adsorption and found to be $120 \text{ m}^2/\text{g}$, which is 150 times greater than $5\mu\text{m}$ diameter iron powder commercially available (Aldrich Chemicals). The sonochemically produced amorphous iron powder sinters at unusually low temperatures. Upon treatment at 350°C , the amorphous powder becomes metallic in color and the scanning electron micrographs show loss of porosity and growth of 50 nm crystallites. This is the case when ultrasonic irradiation is done at low vapor pressure and with a dissolved gas that has a low thermal conductivity and a large ratio of the heat capacities cp/cv .

Again, complete ligand dissociation leading to the formation of metallic glass powders occurs when the cavitation collapse is most extreme. This is the case

at low vapor pressure, low thermal conductivity and large ratios of the heat capacities, C_p/C_v . Under these optimum conditions, iron atomic emission lines were observed in the sonoluminescence spectra thus confirming the formation of iron atoms during ultrasonic irradiation of $\text{Fe}(\text{CO})_5$.

The magnetic properties of the amorphous iron powder have also been examined. The sonochemically produced iron glass is a soft ferromagnet. It has a very low coercivity of 10 gauss at 25°C. This is a highly desirable property for various magnetic information storage and power transformer applications.

The catalytic activity of the amorphous iron powder was probed with two commercially important reactions: the Fischer-Tropsch process (i.e., hydrogenation of CO) and the hydrogenolysis and dehydrogenation of saturated hydrocarbons. The conversion of carbon monoxide and hydrogen to low molecular weight alkanes occurred at very low reaction temperatures (200°C). The amorphous powder was roughly ten times more reactive per gram than 5 μm diameter crystalline iron powder. The hydrogenolysis and dehydrogenation of cyclohexane was about 100 times more efficient at 250°C for the sonochemically produced amorphous iron compared to crystalline iron. The ratio of dehydrogenation to hydrogenolysis depended on temperature, but could be made as large as 0.6. It is believed that the high surface area of the amorphous iron accounts for much of the increase in chemical reactivity. As expected, crystallization and sintering of the metallic glass powders at >300°C significantly decrease their catalytic activity.

The above preferred embodiments and examples are given to illustrate the scope and spirit of the present

invention. These embodiments and examples will make apparent, to those skilled in the art, other embodiments and examples. These other embodiments and examples are within the contemplation of the present invention. Therefore, the present invention should be limited only by the appended claims.

WHAT IS CLAIMED IS:

1. A process for preparing an amorphous metal comprising irradiating a volatile organometallic or inorganic compound with high intensity ultrasound for a time and conditions sufficient to convert the organometallic or inorganic compound into the amorphous metal.

2. The process according to Claim 1 wherein said process is carried out at low vapor pressure in an inert atmosphere.

3. The process according to Claim 1 wherein said low volatile organometallic or inorganic compound is present as a liquid.

4. The process according to Claim 1 wherein, said organometallic or inorganic compound is present in a solution.

5. The process according to Claim 4 wherein said solution contains an alkane.

6. The process of making an amorphous metal comprising:

- (a) preparing a solution of a volatile organometallic or inorganic compound in a low volatility solvent;
- (b) flushing said solution with an inert gas;
- (c) subjecting said solution to ultrasonic irradiation;

- (d) irradiating said solution for a time and conditions sufficient to convert all of the said organometallic or inorganic compound into said amorphous metal; and
- (e) separating said solution and amorphous metal under an inert atmosphere.

7. The process according to Claim 6 wherein said process is carried out at low vapor pressure.

8. The process according to Claim 6 wherein said low volatility solvent is an alkane.

9. The process according to Claim 5 or 8 wherein said alkane is decane.

10. The process according to Claim 1 or 6 wherein said volatile organometallic compound is a metal carbonyl.

11. The process according to Claim 10 wherein said metal carbonyl is $\text{Fe}(\text{CO})_5$, $\text{Cr}(\text{CO})_6$, $\text{Mo}(\text{CO})_6$, $\text{W}(\text{CO})_6$, $\text{Mn}_2(\text{CO})_{10}$ or $\text{Ni}(\text{CO})_4$.

12. The process of making an amorphous metal according to Claim 1 or 6 wherein said volatile inorganic compound is TiCl_4 or $\text{Zr}(\text{BH}_4)_4$.

13. The process of making an amorphous metal according to Claim 1 or 6 wherein said volatile organometallic compound is $\text{Pd}(\text{allyl})_2$.

14. Substantially pure amorphous metal.

15. The substantially pure amorphous metal of Claim 14 wherein the metal is Fe, Cr, Mo, W, Mn, Ni, Ti, Zr or Pd.

16. A catalyst for the hydrogenolysis and dehydrogenation of saturated hydrocarbons comprising the substantially pure amorphous metal of Claim 14.

17. A catalyst for the Fischer-Tropsch hydrogenation of carbon monoxide comprising the substantially pure amorphous metal of Claim 14.

18. A heterogeneous catalyst comprised of sonochemically produced metallic glasses.

19. A soft ferromagnetic material prepared according to Claims 1 or 6.

20. The soft ferromagnetic material of Claim 19 wherein said material is substantially pure iron.

21. The soft ferromagnetic material of Claim 19 wherein said material is an amorphous metal alloy.

22. An amorphous alloy prepared from the ultrasonic irradiation of solutions containing two or more volatile organometallic or inorganic compounds.

23. An amorphous alloy prepared from the ultrasonic irradiation of solutions containing volatile organometallic or inorganic compounds and volatile main group compounds.

24. An amorphous alloy according to Claim 23 wherein the main group compound contains boron, carbon, nitrogen, silicon, phosphorous, sulfur, arsenic, selenium, antimony, tellurium or halide.



FIG. 1

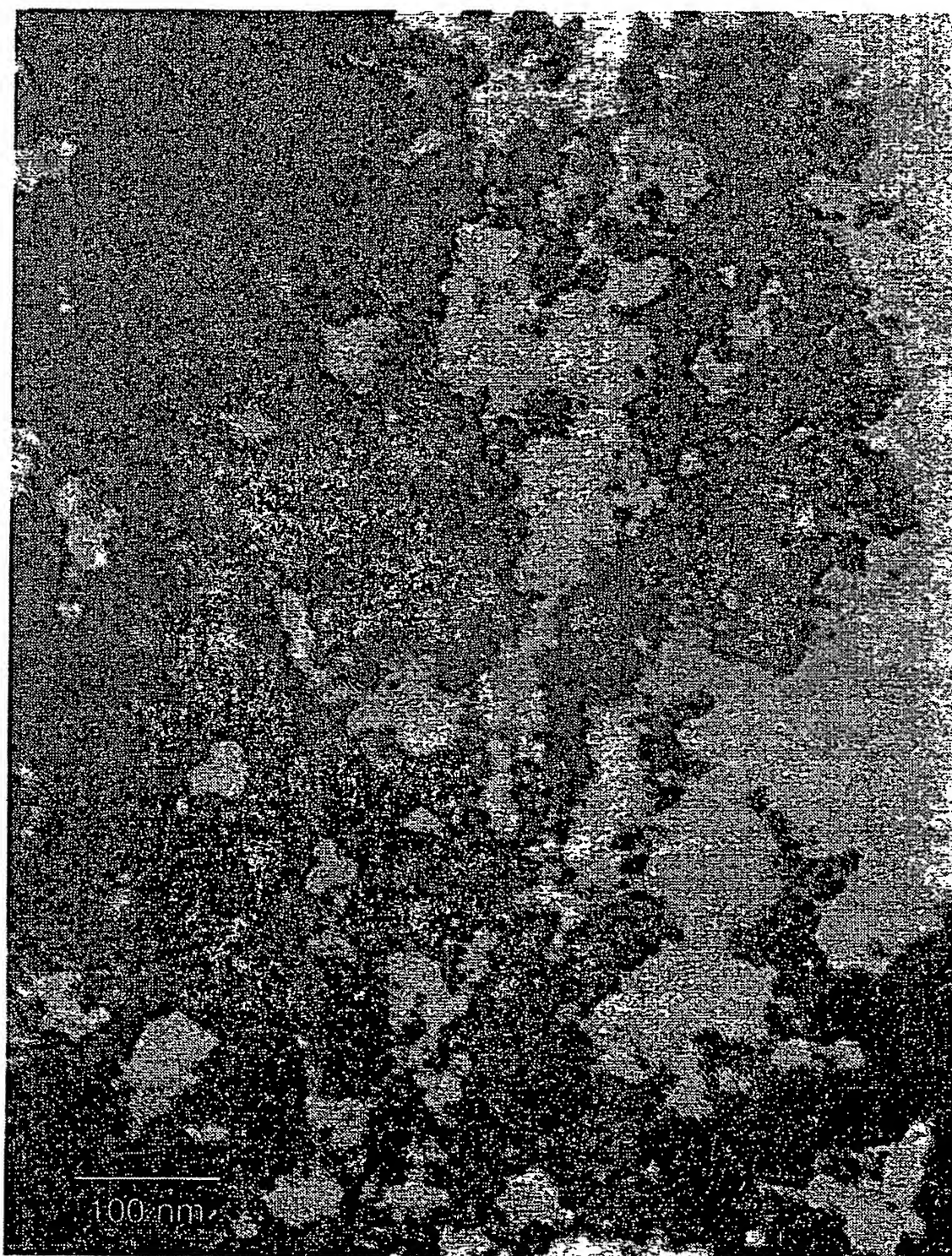
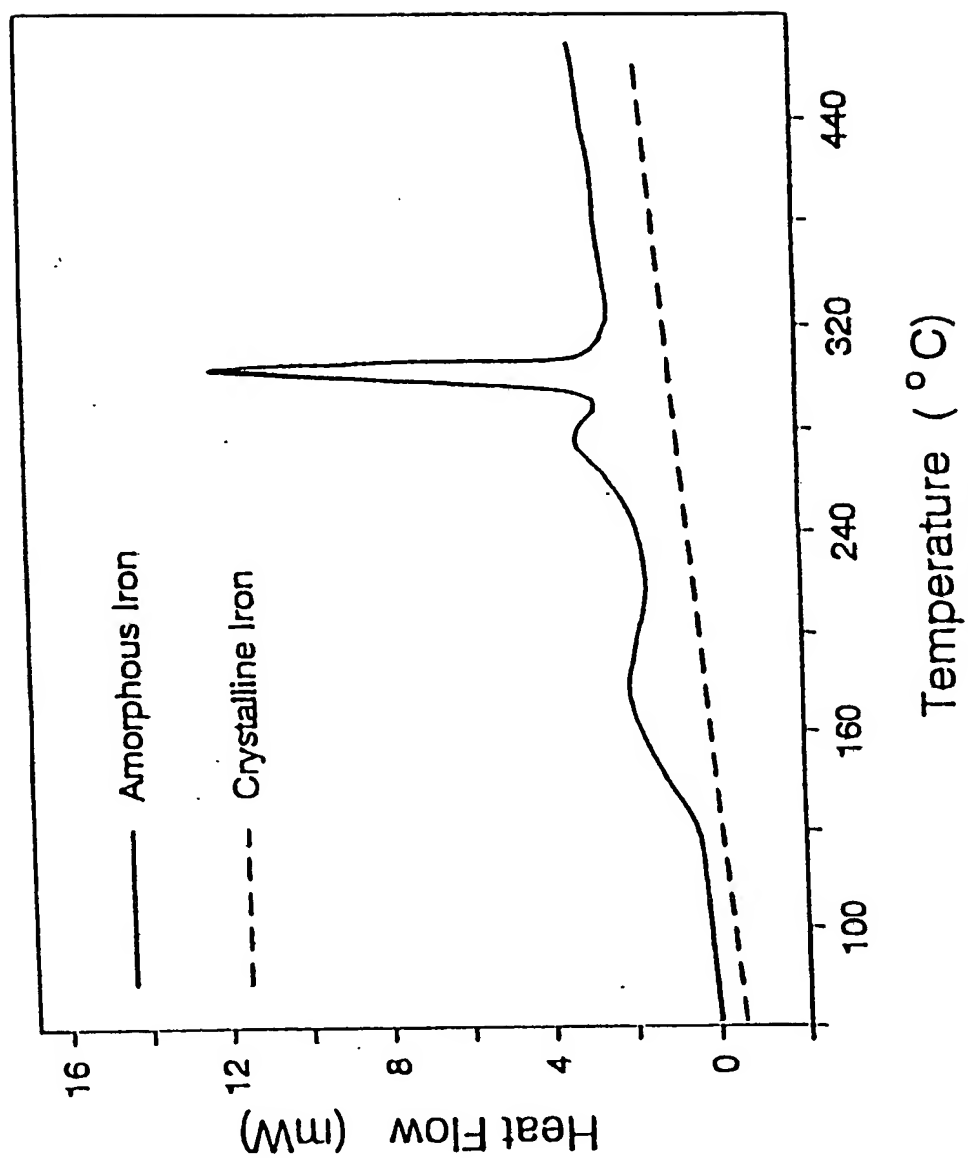


FIG. 2
2/4

SUBSTITUTE SHEET



Temperature (°C)

FIG. 3

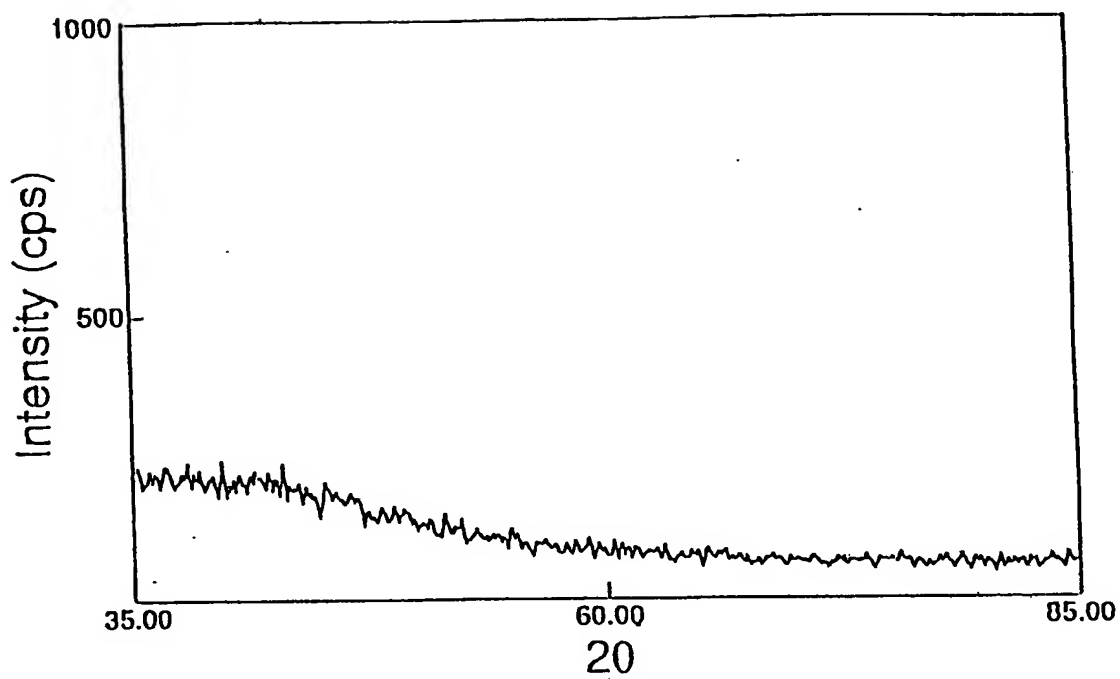


FIG. 4a

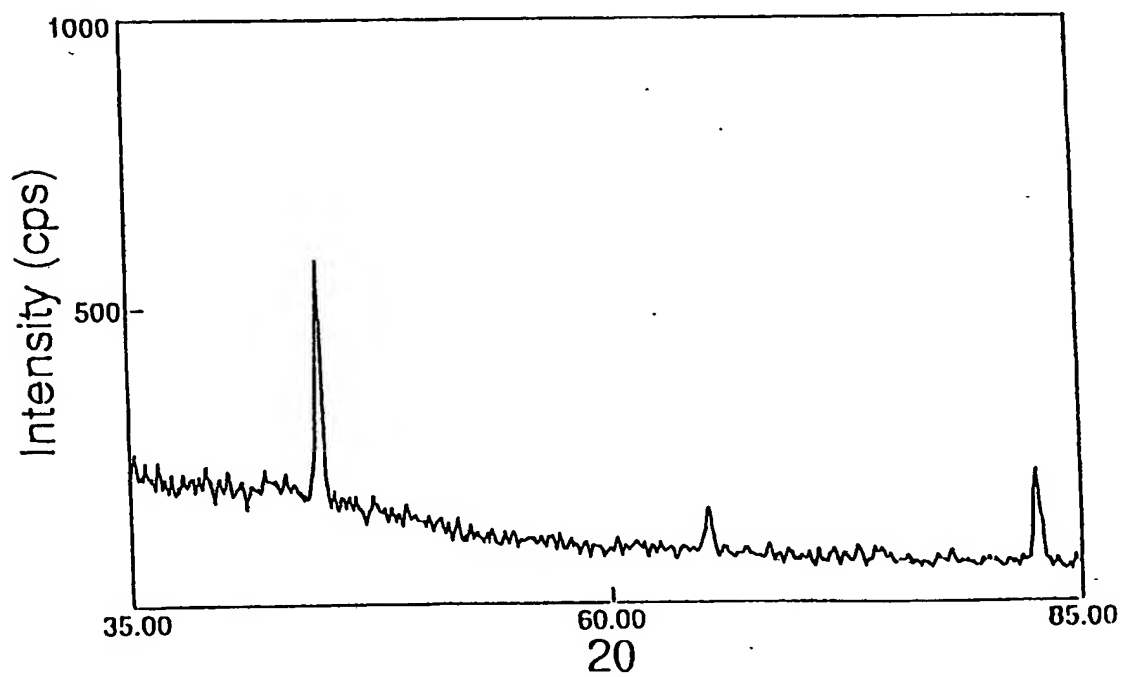


FIG. 4b

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 92/08133

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ⁵ - According to International Patent Classification (IPC) or to both National Classification and IPC IPC5: B 01 J 35/00, B 05 B 17/06, B 22 F 9/30, H 01 F 1/153		
II. FIELDS SEARCHED Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
IPC5	B 01 J; B 05 B; B 22 F; C 22 C; C 22 F	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category *	Citation of Document, ¹¹ with Indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X	SCIENTIFIC AMERICAN, vol. 260, No. 2, February 1989, Suslick K.S : "The Chemical Effects of Ultrasound ", page 66 - page 68, especially page 68, column 3, line 30 - line 35	1,14-24
A	--	2-13
X	EP, A1, 0423627 (STUDIENGESELLSCHAFT KOHLE MBH) 24 April 1991, see page 2, line 1 - page 4, line 41; figures 1-3	14-21
A	--	1-13,22,23,24
A	EP, A1, 0147581 (STUDIENGESELLSCHAFT KOHLE MBH) 10 July 1985, see page 3, line 10 - line 21; page 7, line 1 - line 4	1-24
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<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>* Special categories of cited documents:¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance, the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"Z" document member of the same patent family</p> </div> </div>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
7th January 1993	20. 01. 93	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	Nils Engnell	

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A, T	EP, A1, 0469463 (STUDIENGESELLSCHAFT KOHLE MBH) 5 February 1992, see page 2, line 1 - page 4, line 11; page 7, line 44 - line 50 —	1-24
A	US, A, 2674528 (H. BELLER ET AL) 6 April 1954, see column 2, line 24 - line 50 — ————— (1-24

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO. PCT/US 92/08133**

SA 65250

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on 02/12/92
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A1- 0423627	24/04/91	CA-A- 2027257	15/04/91
		DE-A- 3934351	18/04/91
		JP-A- 3134106	07/06/91
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